Mechanochemistry

DOI: 10.1002/anie.200906583

Ion- and Liquid-Assisted Grinding: Improved Mechanochemical Synthesis of Metal–Organic Frameworks Reveals Salt Inclusion and Anion Templating**

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The development of metal–organic frameworks (MOFs) as functional materials[1] has prompted the search for rapid and economical approaches for their synthesis. Conventional solvothermal[2] approaches to MOF synthesis are now joined by sonochemistry,[3] microwave synthesis,[4] and mechanosynthesis.[5] We have demonstrated that liquid-assisted grinding (LAG)[6,7] can be utilized to construct MOFs with moderate porosity from a readily accessible metal oxide, such as ZnO, at room temperature.

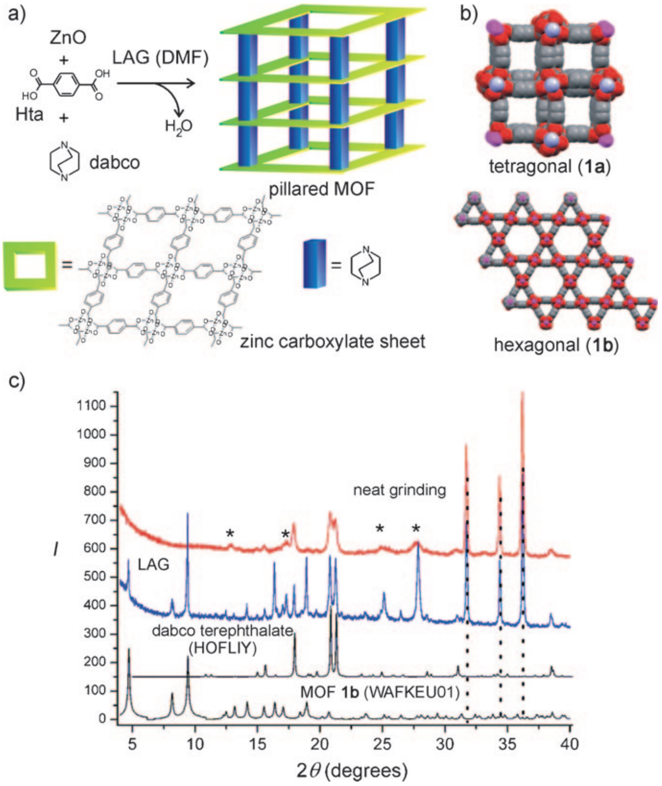

Figure 1. a) Expected MOF **1** assembly; b) MOF isomers **1a** and **1b**; red O, gray C, blue N, purple Zn. c) PXRD patterns (top to bottom): 60 min neat grinding (red; no reaction), 60 min LAG (blue; partial reaction), simulated pattern for the dabco-Hta salt and for **1b** (in square-root scale). Dotted lines indicate reflections of ZnO; reflections of residual Hta are labeled "*".

We now demonstrate that catalytic amounts of simple salts can accelerate such synthesis and, through templating effects not previously seen in mechanosynthesis, direct the structure of the product. As a result, ionic guests become included in a neutral MOF, as established by powder X-ray diffraction (PXRD), FTIR-attenuated total reflection (ATR), and magic-angle spinning (MAS) solid-state NMR spectroscopy. We introduce this improved mechanochemical approach, designated ion- and liquid-assisted grinding (ILAG), in the construction of MOFs based on terephthalic acid (Hta) (Figure 1 a).[8] Solvothermal assembly of zinc nitrate, Hta, and 1,4-diazabicyclo[2.2.2]octane (dabco) is known to provide the MOF $[Zn_2(ta)_2(dabco)]$ (**1**).[9] This framework belongs to the family of pillared MOFs, investigated for fuel separation, polymerization, and gas storage.[9,10] A number of isomers of **1** are known, several of which are tetragonal (jointly designated as **1a**)[10a] and one is hexagonal, based on a Kagome lattice (**1b**, CCDC code WAFKEU01;[11] Figure 1 b). We first attempted mechanosynthesis of **1** by grinding ZnO, Hta, and dabco in the stoichiometric ratio 1:1:0.5. As revealed by PXRD, neat grinding for 60 min only provided the dabco-Hta salt.[12] However, 60 min LAG with DMF resulted in partial reaction to form **1b** (Figure 1 c).[11] Formation of **1b** is surprising, as solvothermal synthesis in DMF exclusively provides **1a** MOFs. Since solvothermal synthesis is usually conducted using zinc nitrate, we suspected that the discrepancy could be caused by nitrate ions. Consequently, we conducted the LAG reaction with a small amount of $NaNO_3$ (20 mg, weight fraction of solid reactants $w = 12\,\%$).

After grinding for 20 min, PXRD indicated almost complete disappearance of ZnO to form a mixture of **1a** (CCDC code HEGKAP)[10a] and **1b**.[13] Other metal nitrates (KNO_3, $RbNO_3$, and $CsNO_3$) and NH_4NO_3 also induced

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[**] The Herchel Smith fund is acknowledged for a research fellowship (T.F.). M.J.D. and D.G.R. acknowledge BBSRC for funding. Financial support provided by the Bundesministerium für Bildung und Forschung (BMBF) and the Fonds der Chemischen Industrie (FCI) is acknowledged (I.H., R.E.D.). Prof. W. Jones, University of Cambridge, is acknowledged for helpful discussions.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200906583.

partial formation of **1a** upon ILAG, with the amount of **1a** increasing with grinding time. A Le Bail fit of PXRD patterns revealed that 45 min grinding with KNO_3 or NH_4NO_3 gave almost pure **1a** (Figure 2a).[14–17] In contrast, ILAG with Na_2SO_4, $(NH_4)_2SO_4$, or K_2SO_4 quantitatively provided **1b** in 30 min (Figure 2b), with no detectable amount of **1a** even after 1 h grinding. MOF formation was confirmed by ^{13}C solid-state NMR.[10c]

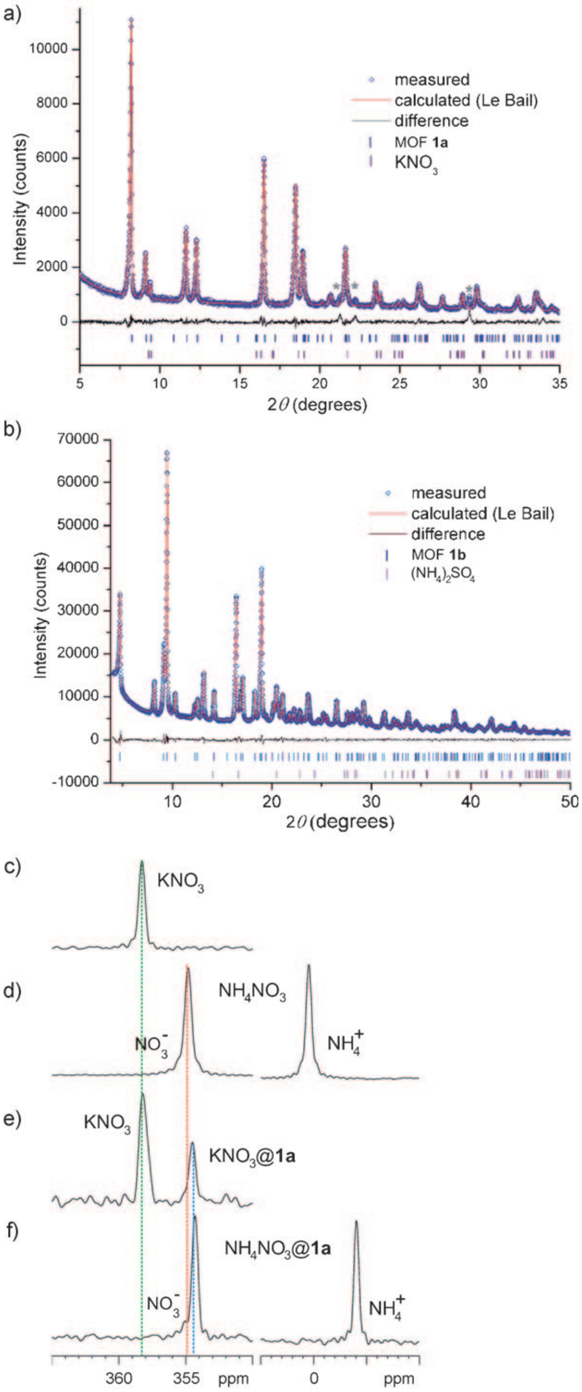

Figure 2. Le Bail fits of PXRD patterns of MOFs prepared using: a) KNO_3, 45 min ILAG and b) $(NH_4)_2SO_4$, 30 min ILAG. Reflections that could not be assigned are indicated by "*". ^{15}N DP-MAS NMR spectra of: c) $K^{15}NO_3$; d) $^{15}NH_4{}^{15}NO_3$; e) **1a** prepared using $K^{15}NO_3$ and f) **1a** prepared using $^{15}NH_4{}^{15}NO_3$. Colored dotted lines approximate the positions of the nitrate ^{15}N NMR signal in pure $K^{15}NO_3$ (green), $^{15}NH_4{}^{15}NO_3$ (red), and ILAG products (blue).

That nitrates and sulfates induce the formation of **1a** or **1b**, respectively, suggests an anion-templating mechanism.[18] PXRD analysis revealed that KNO_3 is not observed in the product if its quantity is below 7 mg ($w \approx 5\,\%$). In contrast, NH_4NO_3 could not be detected even at 22 mg loadings ($w \approx 13\,\%$). These observations support the anion-templating mechanism, and suggest that different salts become included in the MOF in variable amounts.[16–18]

To investigate possible salt inclusion in a neutral MOF, we conducted ILAG with ^{15}N-labeled KNO_3. Direct-polarization (DP) MAS NMR of the product revealed two signals: one at $\delta = 359$ ppm, corresponding to excess pure salt, and one at $\delta = 354$ ppm, tentatively assigned to MOF-included ions (Figure 2c–f). For $^{15}NH_4{}^{15}NO_3$, the $^{15}NO_3$ signal shifted from $\delta = 355$ to 354 ppm, and the $^{15}NH_4{}^+$ signal from $\delta = 0.50$ ppm to -4.0 ppm, suggesting the inclusion of the anion and cation. A similar result was obtained with $Na^{15}NO_3$, where a broad peak centered at $\delta = 356$ ppm was observed after ILAG.[19]

Sulfate salts used to accelerate the synthesis of **1b** were always detected in the PXRD pattern of the product, suggesting a low level of inclusion and a high templating efficiency of $SO_4{}^{2-}$ ions. Indeed, Na_2SO_4, K_2SO_4, or $(NH_4)_2SO_4$ induced quantitative formation of **1b** even at loading levels as low as $w = 0.3\,\%$. Sulfate inclusion was verified indirectly by ^{15}N DP-MAS NMR. The spectrum of **1b** obtained using $(^{15}NH_4)_2SO_4$ ($w = 0.7\,\%$) revealed two peaks (Figure 3a). While the major peak at $\delta = 1.8$ ppm belongs to pure $(^{15}NH_4)_2SO_4$, the minor peak at $\delta = -1.5$ ppm is interpreted as MOF-included salt.

Templating and salt inclusion by ILAG are not limited to nitrates and sulfates (Table 1). A particularly interesting target is the $ReO_4{}^-$ ion, an important analogue of the radioactive pollutant $^{99}TcO_4{}^-$.[20] The inclusion of NH_4ReO_4 and $NaReO_4$ in **1b** is evident by the absence of salt reflections in the PXRD pattern and by the appearance of a new absorption band at 910 cm^{-1} in the FTIR spectra (Figure 3b). This band does not appear in **1a** or **1b** prepared using other salts, and is consistent with one of four $ReO_4{}^-$ vibrational modes expected between 840 and 980 cm^{-1}.[21] In pure salts this band is broadened by coupling to lattice vibrations and we interpret its sharpening as anion inclusion in **1b**. Inclusion of $NaReO_4$, NaCl, and $Na_2S_2O_3$ in MOFs is also inferred from the ^{23}Na MAS NMR spectra of ILAG products, which differ from those of pure salts (Figure 3c).

Formation of MOFs under mechanochemical conditions is accelerated and directed by small amounts of salts. To our knowledge, this is the first demonstration of anion templating in mechanosynthesis,[7,22] and of using additives to enhance MOF mechanosynthesis.[5] We have identified salts that are specific for a particular product (e.g. NH_4NO_3 or K_2SO_4), as well as those that exhibit lesser specificity (e.g. K_2MoO_4 or $Na_2S_2O_3$). While the high templating activity of sulfates is an attractive synthetic tool, it also demonstrates surprising sensitivity of mechanosynthesis to impurities.[23] That the activity of nitrate ions is affected by the counterion (e.g. $NaNO_3$ vs. KNO_3) suggests that templating involves ion pairs

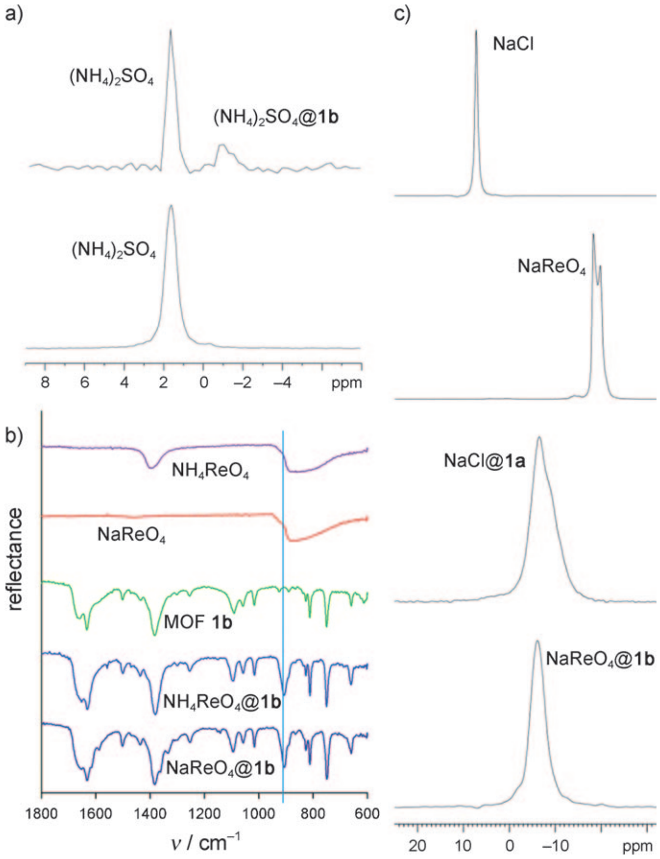

Figure 3. a) ^{15}N DP-MAS NMR spectra of pure (^{15}NH$_4$)$_2$SO$_4$ (bottom) and a sample of **1b** prepared by LAG with (^{15}NH$_4$)$_2$SO$_4$ (top, $w = 0.7\%$); b) FTIR-ATR spectra of (top to bottom): NH$_4$ReO$_4$, NaReO$_4$, **1b** with DMF guest, **1b** obtained by ILAG with NH$_4$ReO$_4$, and **1b** obtained by ILAG with NaReO$_4$; the vertical line marks the 910 cm^{-1} band; c) ^{23}Na DP-MAS NMR spectra (top to bottom) of: NaCl, NaReO$_4$, **1a** obtained by ILAG with NaCl, **1b** obtained by ILAG with NaReO$_4$.

Table 1: Results of MOF synthesis using different salt additives.[a]

Salt	Product	Salt	Product
NaNO$_3$	**1a** and **1b**	Na$_2$S$_2$O$_3$[b]	**1a** and **1b**
KNO$_3$	**1a**	K$_2$MoO$_4$	**1a**[c] and **1b**[d]
NH$_4$NO$_3$	**1a**	NaCl	**1a**
Na$_2$SO$_4$	**1b**	NaNO$_2$	**1a**
(NH$_4$)$_2$SO$_4$	**1b**	NaReO$_4$	**1b**
K$_2$SO$_4$	**1b**	NH$_4$ReO$_4$	**1b**

[a] Performed by 30 min ILAG with 20 mg ($w = 12\%$) of added salt. [b] 60 min ILAG provides only **1a**. [c] Major product. [d] Minor product.

or clusters.[16] Although solution templating of MOFs has been investigated, such studies have focused on charged networks.[24] Our results suggest that templating by ions could be an important factor in the synthesis of neutral MOFs, as well as that salts become included in MOFs under mechanochemical conditions. Both observations are attractive for applications in solid-state synthesis, anion recognition, or conductivity. We are now exploring the general synthetic applicability of ILAG and the mechanism of ion inclusion by using solid-state NMR spectroscopy.

Experimental Section

All LAG reactions were performed at 0.5 mmol scale, by placing a mixture of solid reactants ZnO (40 mg), Hta (80 mg), and dabco (28 mg) into a 10 mL stainless steel jar, along with 120 μL of DMF as the grinding liquid and two 7 mm diameter stainless steel balls. The amount of salt added was varied between 1–20 mg, except in the case of (^{15}NH$_4$)$_2$SO$_4$, where amounts as low as approximately 0.4 mg (2 small crystals, $w \approx 0.3\%$) were also used. The mixture was then ground for 20–60 min in a Retsch MM200 grinder mill operating at 30 Hz. During grinding the mill was flushed with a strong stream of air, to keep the average temperature of the jars between 20 °C and 25 °C.

Received: November 22, 2009

Keywords: ions · mechanochemistry · metal–organic frameworks · solid-state reactions · sustainable chemistry

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